



USE OF MINERAL ACIDS FOR NEUTRALISATION OF BAUXITE RESIDUE PRIOR TO METAL RECOVERY BY ACIDIC LEACHING

MSCA-ETN REDMUD PROJECT

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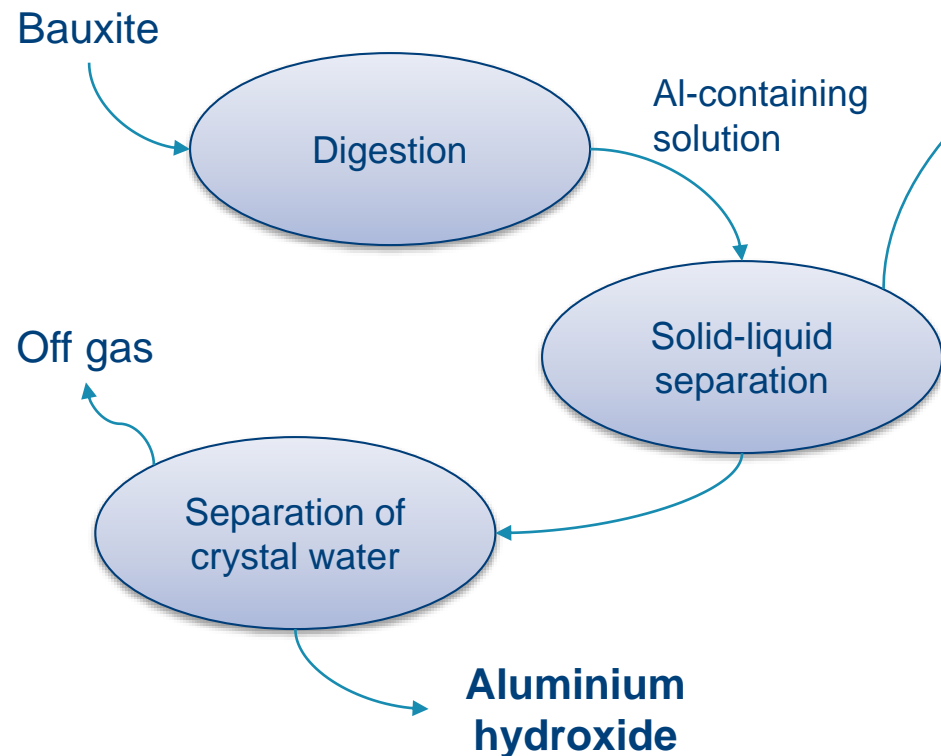
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1. TURNING THE BAUXITE RESIDUE INTO AN OPPORTUNITY

Principle flowchart of Bayer process



**Bauxite residue
(red mud)
pH > 10**

- Production: 1.5×10^8 tonnes/year^[1]
- Inventory: 2.7×10^9 tonnes^[2]



[1] Evans, (2016). J. Sustain. Met. 2, 316–331.

[2] Klauber et al., (2011). Hydrometallurgy 108, 11–32

1. TURNING THE BAUXITE RESIDUE INTO AN OPPORTUNITY

Major chemical components in **Greek bauxite residue**

Element	Concentration, wt%	Mineral phase
Fe	33	Hematite, goethite
Al	10	Gibbsite, diaspore, bayerite
Ca	6	Calcite, calcium silicates, calcium-aluminium silicate
Si	3	Silicates
Ti	3	Rutile
Na	2	Sodalite, cancrinite
Loss on ignition	8.5	Carbon dioxide, crystalline water

Selected rare-earth elements composition in the bauxite residue^[3]

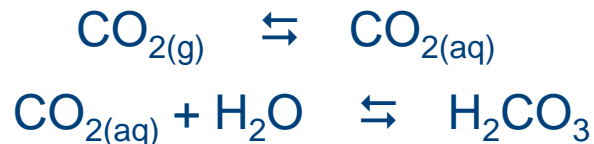
Element	Concentration, g/tonne
Sc	121 ± 10
Y	76 ± 10
La	114 ± 15
Nd	99 ± 7

>90% of the economical value of REEs in bauxite residue^[3]

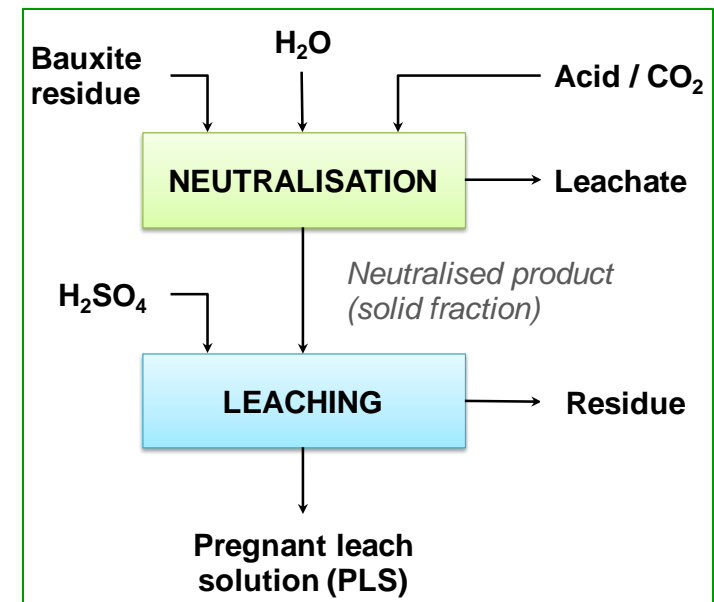
[3] Borra et al. (2015). Min. Eng. 76, 20-27

2. METAL RECOVERY BY ACIDIC LEACHING

- Major and minor elements can be recovered with HCl , HNO_3 or H_2SO_4 ^[5]
- Part of the acid must be used for the neutralisation of the alkaline products left behind after the Bayer process.
- High acid consumption.
- Carbonic acid (H_2CO_3) is an inexpensive and safe technology for bauxite residue neutralisation.



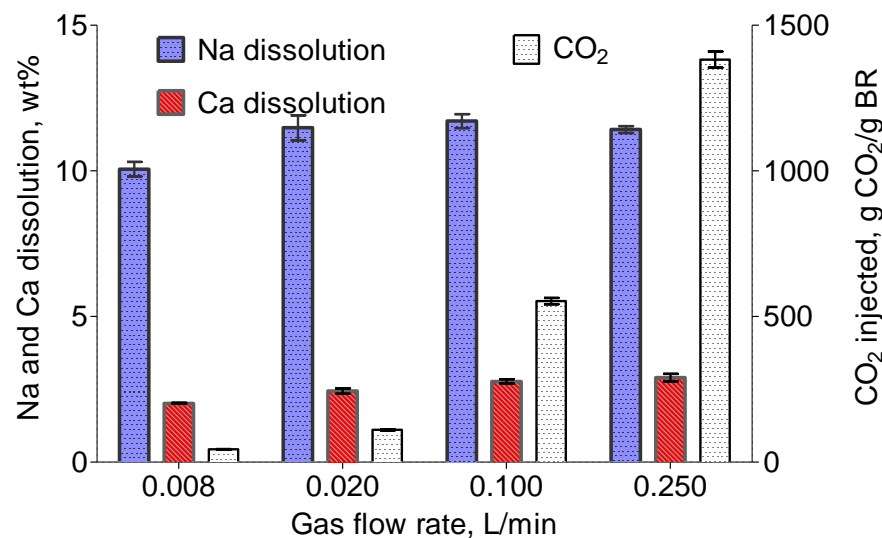
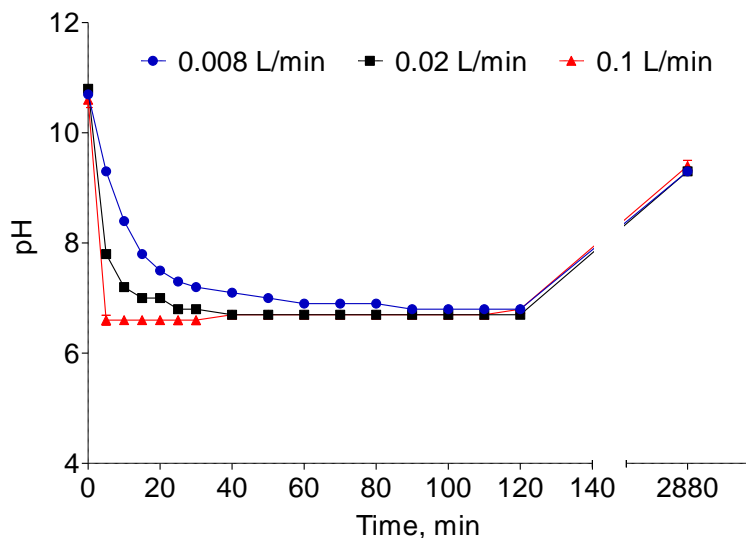
- H_2CO_3 may reduce material's alkalinity → reduction of acid consumption during metal recovery by acidic leaching.



[5] Borra et al. (2016). J. Sustain. Met., 4, 365-386

2. NEUTRALISATION OF BAUXITE RESIDUE WITH H_2CO_3

CO_2 gas flow rate effect (T : 25 °C, L/S : 5):

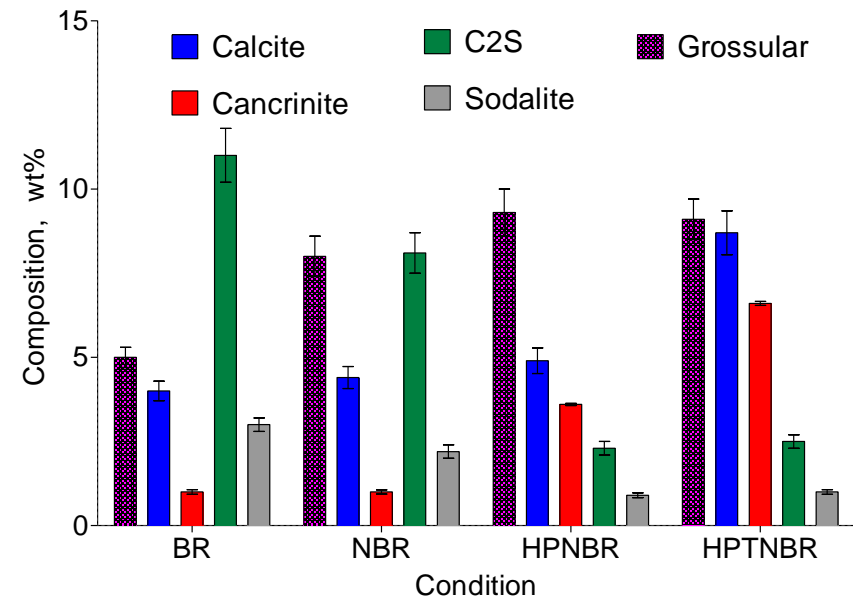
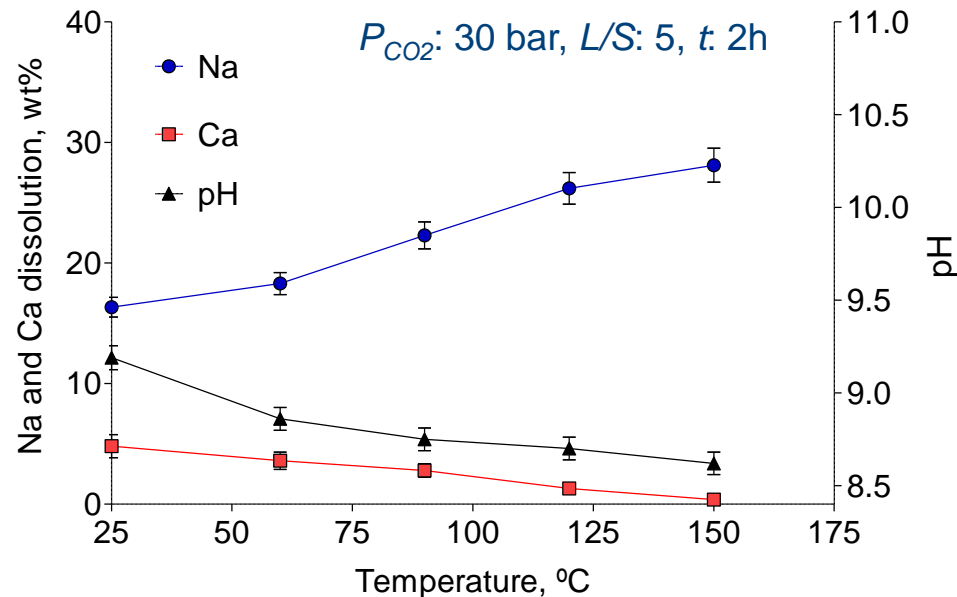


- pH reduction from 10.7 to ~6.8
- Rebound of the pH due to unreacted hydroxide compounds.

- About 8 wt% of Na is readily soluble in water.
- 2 to 4 wt% of Na reacts with the H_2CO_3 .

2. NEUTRALISATION OF BAUXITE RESIDUE WITH H_2CO_3

Neutralisation with high pressure:



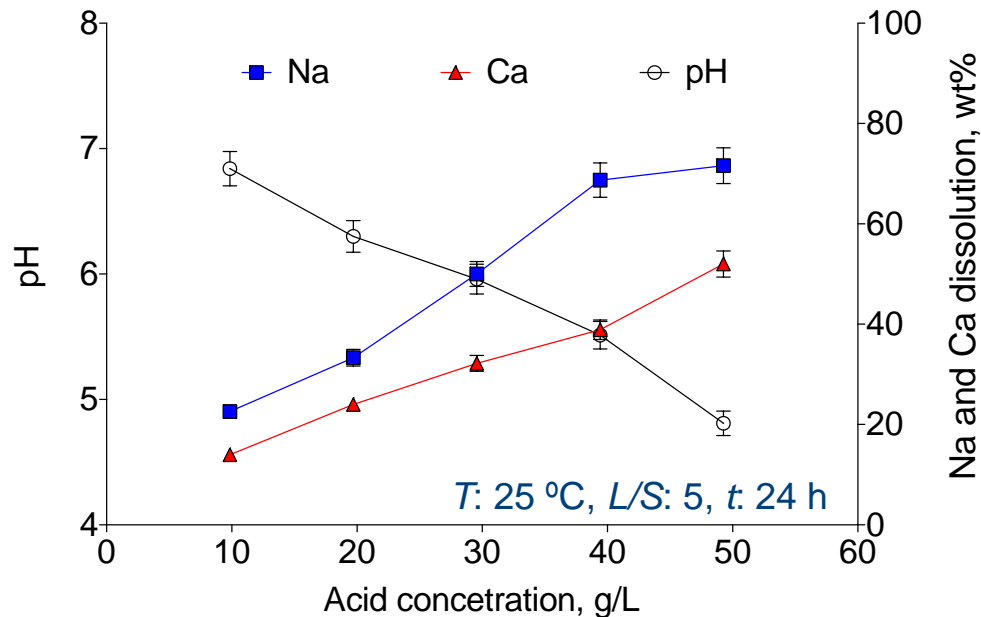
- High Na dissolution with the increase of temperature and P_{CO_2} .

BR: non-neutralised bauxite residue, NBR: q_{CO_2} : 0.25 L/min, T : 25 °C
 HPNBR: P_{CO_2} : 30 bar, T : 25 °C; HPTNBR: P_{CO_2} : 30 bar, T : 150 °C

- SiO_2 solubility decrease with high dissolution of sodium^[6].

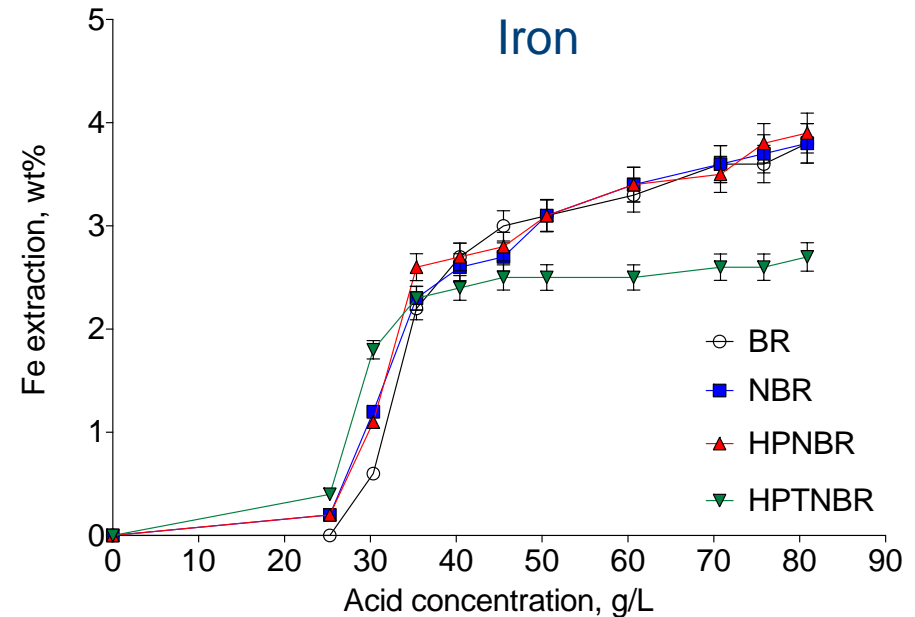
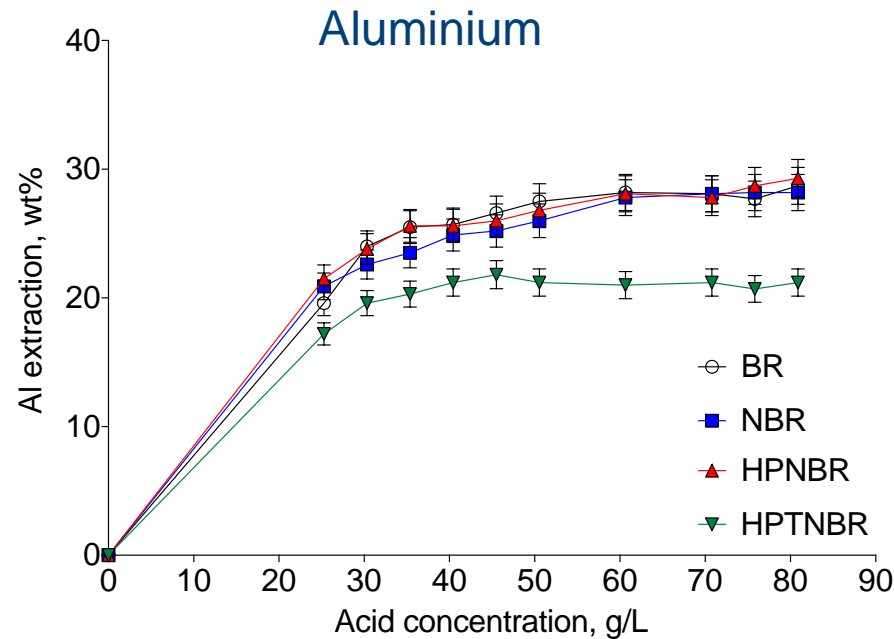
[6] Zheng et al. (1998). J. Chem. Eng. Data 43, 312–317

3. NEUTRALISATION OF BAUXITE RESIDUE WITH HCl



- Higher dissolution of Na and Ca in comparison to neutralisation with H_2CO_3 .
- The price of the acid may reach a value of up to 200 USD/tonne.
- CO_2 can be obtained from the gas emissions generated during the alumina production (Bayer process).

4. LEACH OF NEUTRALISED BAUXITE RESIDUE (H_2SO_4 , 25 °C, L/S: 10, 24 h)

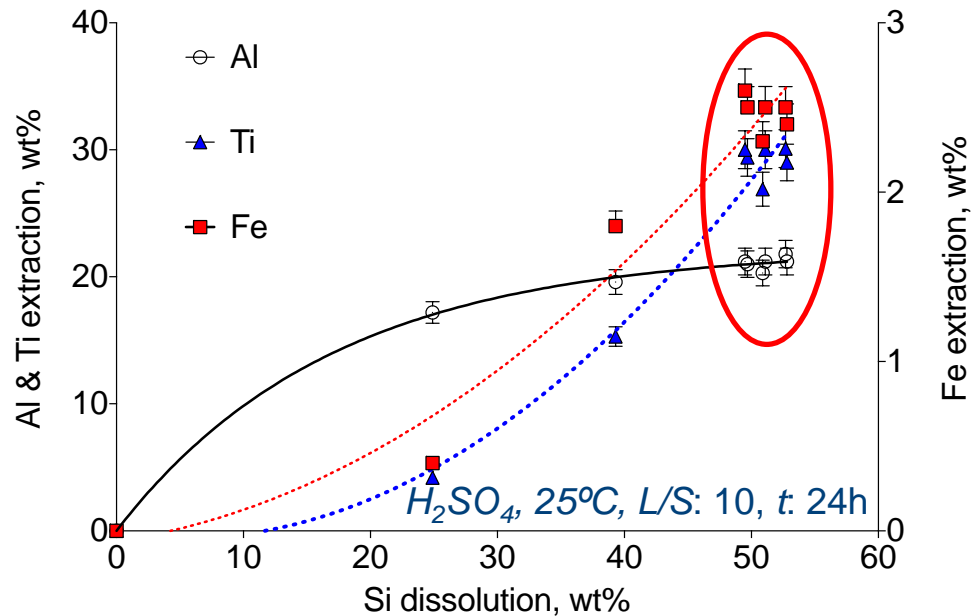


- Low metal recovery (also for titanium) caused by the chemical transformation of calcite into bassanite and the polymerisation of amorphous silica.

BR: non-neutralised bauxite residue, NBR: q_{CO_2} : 0.25 L/min, T : 25 °C
 HPNBR: P_{CO_2} : 30 bar, T : 25 °C; HPTNBR: P_{CO_2} : 30 bar, T : 150 °C

4. LEACH OF NEUTRALISED BAUXITE RESIDUE (H_2SO_4 , 25 °C, L/S: 10, 24 h)

Bauxite residue sample neutralised at 150 °C and P_{CO_2} : 30bar

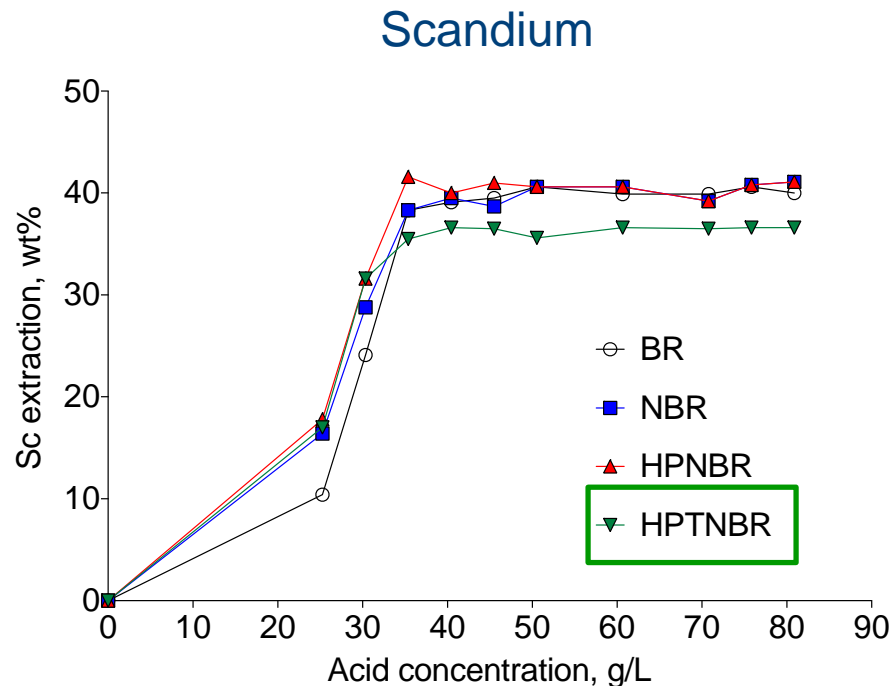


- Extraction of Al, Fe or Ti is limited by 50 wt% of Si dissolution.
- An increase in silica dissolution leads to a larger supersaturation of silicic acid → driving force for polymerization^[7,8]

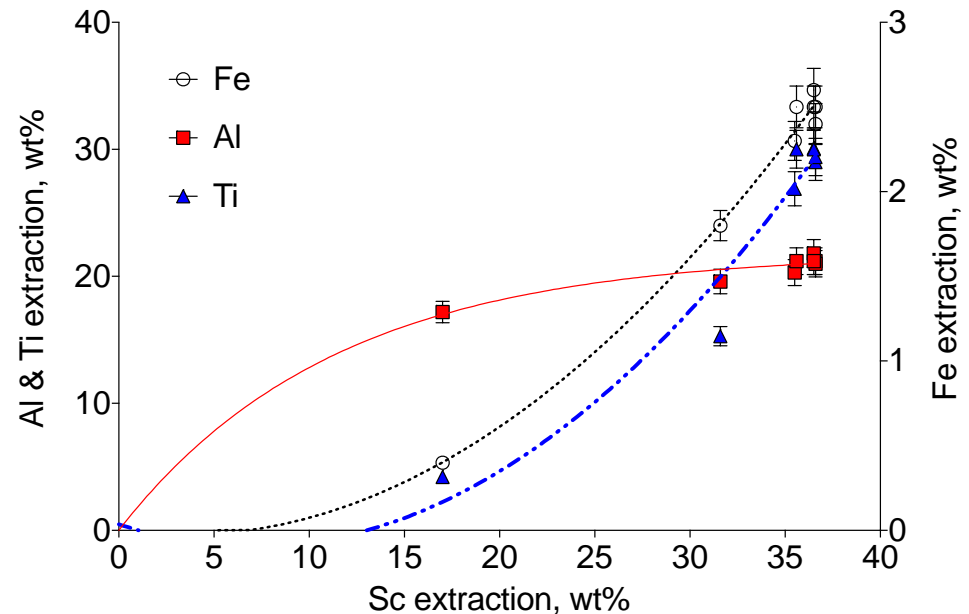
[7] Hamouda et al. (2014). *Energies* 7, 568–590

[8] Tobler et al. (2009). *Geochim. Cosmochim. Acta* 73, 5377– 5393

4. LEACH OF NEUTRALISED BAUXITE RESIDUE (H_2SO_4 , 25 °C, L/S: 10, 24 h)



Dissolution after acidic leaching of HPTNBR



Low Sc recovery due to its chemical association with major elements.

HPTNBR: P_{CO_2} : 30 bar, T : 150 °C, L/S : 5, t : 2h.

5. NEUTRALISATION-LEACHING VERSUS CONVENTIONAL DIRECT LEACHING

Parameters	Direct leaching ^[3]	Leaching HPTNBR
Scandium extraction, wt%	50	35
Processed bauxite residue per gram of scandium recovered, kg BR/g Sc	17	24
Acid consumption, g H ₂ SO ₄ /kg BR	760	464
Iron concentration in PLS, mg/L	>2000	<900

[3] Borra et al. (2015). Min. Eng. 76, 20-27

4. CONCLUSIONS

Bauxite residue neutralisation:

- Minimum pH obtained after neutralisation with CO_2 was 8.6 → Further pH decrease is limited, because of the chemical association of sodium to the sparsely soluble silicates.

Leach of neutralised bauxite residue:

- Sc recovery reached up to 35 wt% by leaching the highly neutralised bauxite residue → 13% less than direct acidic leaching.
- With the neutralisation-leaching method, more bauxite residue can be processed with a significant low acid consumption and without bringing a significant amount of iron into the solution (<900 mg/L).
- REEs recovery is limited by the presence of Fe and Ti → Recovery of major metals must be done in advance (e.g. via smelting).
- The presence of silica in the leach solution must be avoided in order to avoid polymerization.



<http://www.etn.redmud.org>

Thank you very much for your attention

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